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Research Article

Synthesis of Al_2O_3–SiO_2–MgO ceramics with hierarchical porous structure

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Abstract: A series of asymmetric cordierite ceramics with hierarchical porous structure were prepared and characterized. The macroporous support was obtained from natural raw materials (bauxite, silica sand, kaolinite, talc, and alumina) via ceramic technology. The prepared ceramic discs were characterized by a narrow pore size distribution. The average pore size was about 9.5 μm, and the open porosity was estimated to be 30%. Coating the discs with micro/mesoporous cordierite layer was performed using the sol–gel approach. Three-component sols were obtained from organic or inorganic precursors. Corresponding gels were calcined at 1200 ℃ to form the cordierite structure. The nature of precursor was found to affect the pore volume distribution. Narrow pore volume distribution was observed when organic precursors were used. Another key factor to control the parameters of final material was the drying condition. Supercritical drying of the gels has allowed us to increase the surface area in two orders of magnitude comparing with conventional drying procedure.

Keywords: sol–gel method; aerogels; cordierite; Al_2O_3–SiO_2–MgO; hierarchical porous structure

1 Introduction

The characteristics of porosity (total amount of pores, ratio of closed/open porosity, average pore size and distribution, pore shape) are the properties determining the suitability of ceramic materials for potential applications [1]. For example, micropores are required for adsorption and purification processes (including catalytic purification) of a gaseous or liquid stream, while macropores play a key role in filter cleaning systems, thermal insulators as well as for biomedical applications. A combination of different pore morphologies in a single monolithic matrix extends the properties of the overall system, and subsequently widens significantly its range of application. In aim to perform multiple functions of porous materials, hierarchical porosity could be considered as a means to accomplish these tasks. For example, micro–macro porosity can greatly improve the performance of microporous materials in areas where a component with both catalytic function and high mechanical strength is required. In general, a macroporous ceramic framework offers chemical and mechanical stability, as well as high convective heat transfer, high turbulence, low pressure drop, and a high external mass transfer rate due to

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interconnections between the macropores, while the micro/mesoporous system provides the functionality for a given application [2,3]. A component containing hierarchical porosity typically possesses simultaneously a wide range of desirable characteristics, which include high accessibility, rapid transport of fluids and gases, high selectivity, fast uptake and release, the possibility of rapid thermal cycling, chemical and mechanical stability, and efficient use of volume. Such components are therefore of significant technological interest, and are successfully used in several industrial processes and household products. Fields of its application include catalysis, filtration of liquids or gases, extraction, separation, sorption, and so on [4,5].

In this work, the preparation method for Al_2O_3–SiO_2–MgO ceramics with hierarchical porous structure (Fig. 1) was developed. The macroporous cordierite ceramic support was prepared from natural raw materials (kaolin, bauxite, talc, alumina, and silica sand). The use of natural sources for ceramic synthesis has allowed us to reduce the cost of resulted products. The micro/mesoporous Al_2O_3–SiO_2–MgO layers were prepared by sol–gel method from organic or inorganic precursors under different drying conditions. Xerogels were obtained by drying gels under normal conditions in air. Aerogels were obtained by drying gels under supercritical conditions when the surface tension was eliminated. This technology makes it possible to avoid the collapse of the pore structure during the liquid phase elimination [6].

The choice of initial components and applied approaches has been determined as follows. Cordierite is known to be widely used in metallurgy, mechanical engineering, and chemical industry as refractories, filters, and catalyst support. Theoretical composition of cordierite oxide can be represented as 13.7 wt% MgO, 34.9 wt% Al_2O_3, and 51.4 wt% SiO_2. In a number of studies, pure oxides or salts in stoichiometric ratios are used to obtain cordierite, but more promising is the synthesis from natural materials without any additional pretreatment. Starting materials used in this work are similar in mineral and chemical composition if comparing with those applied in the refractory and ceramic industry [7]. The desired phase composition and porosity after sintering can be provided by selecting the optimum ratio of the starting natural components.

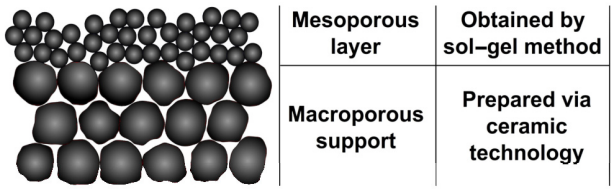


Fig. 1 Schematic image of cordierite ceramics with hierarchical porous structure.

The sol–gel technique is known to be useful for processing a large number of technologically important glasses, glass–ceramics, and crystalline ceramics, mainly because of its ability to generate stoichiometric materials of high purity with appropriate control over both particle and pore sizes [8]. The advantage of sol–gel technology with reference to the formation of micro/mesoporous layers of ceramic materials consists in the possibility of variation of the sol composition, presence of binding, softening, and modifying additives, which can be applied to modify the porous layer properties [9–14]. The key factors to control the surface porosity are the size of initial sol particles, sol concentration and composition, viscosity of the composition, pH, and conditions of thermal processing [11]. These factors affect the stability of sol, thus providing the minimum particle sizes along with the narrowest pores of forming layers.

The sol–gel synthesis attracts much interest for preparation of mesoporous layers due to possibility of parameters of final ceramics to be easily controlled while varying the process condition. Thus, the nature of organic solvent (methanol, ethanol, 2-propanol, 2-butanol) and alcoholate group (CH_3O-, C_2H_5O-, C_3H_7O-, etc.), the rate of water addition as well as pH influence the yield and morphology of the product [15,16]. A variety of sol–gel approaches, which have started from the similar composition of a batch, provide a number of products different in properties [17,18].

Thereby, the combination of ceramic technology with sol–gel approaches permits obtaining of the materials with interpenetrative architecture of the layers which are similar in phase composition but different in particle size and textural characteristics. Hierarchical porous structure within one material provides the reduction of diffusion barriers as well as optimal distribution and accessibility of active components in catalytic applications [19,20].

2 Experimental

Macroporous cordierite ceramic support was prepared from natural raw materials as described in Ref. [21]. Components required to obtain the cordierite with formula $Mg_2Al_4Si_5O_{18}$ were mixed in the stoichiometric

ratio as follows: 43 wt% bauxite, 21 wt% silica sand, and 36 wt% talc, or 52 wt% kaolinite, 36 wt% talc, and 12 wt% alumina. The mixture was ground in a porcelain mortar and subsequently in a KM-1 colloid mill for 3 h. The particle size of obtained powder (20–30 μm) was controlled by laser particle size analyzer FRITSCH Analisette-20. Forming of samples of the membrane discs was performed by the dry pressing in round molds made of stainless steel on an IP-100 press under uniaxial loading. Pressing force was 70 MPa at a loading rate of 0.2–0.3 MPa/s. A 5% aqueous solution of polyvinyl alcohol (PVA) was used as the binder component.

The samples were investigated by differential scanning calorimetry (DSC) to select the sintering temperature. During the calcinations, the ceramic discs were heated up to 700 ℃ with temperature ramping rate of 2 ℃/min and isothermally kept at final temperature for 1 h using Linn High Term HT-1800 furnace. High-temperature treatment was performed isothermally at 1380 ℃for 1 h in air. In this case, heating and cooling rates were 7 ℃/min.

The micro/mesoporous cordierite layers have been prepared by means of a sol–gel technology. The synthesis of alumina, magnesia, and silica sols was performed from organic or inorganic precursors by using standard procedures. Instability of three-component sol systems has forced us to use the separate preparation procedures of individual sols in most cases, and then mix them in an appropriate order.

Inorganic alumina sol was prepared by hydrolysis of $AlCl_3 \cdot 6H_2O$ in ammonia solution at room temperature. Magnesium chloride was added when the pH value was equal to 5, and then joint hydrolysis by ammonia solution was continued until pH reached the value of 5.5. As a result, stable opalescent joint sol of aluminum and magnesium hydroxides was formed. This sol was labeled as Al_2O_3 (inorg). In order to prepare the silica sol, 60 g of $Na_2SiO_3 \cdot 9H_2O$ was dissolved in 200 cm^3 at heating, filtered, and then added to 100 cm^3 of concentrated hydrochloric acid mixed with water in equal parts. Then, the solution was subjected to dialysis. The obtained SiO_2 sol (labeled as SiO_2 (inorg)) was added to joint sol of aluminum and magnesium hydroxides.

The organic approach consists of the following steps. In order to obtain alumina sol, toluene was placed into conical flask equipped with dephlegmator [22]. The flask was heated up to 70 ℃, and then aluminum ethoxide was added dropwise. The resulted suspension was stirred for 15 min, and then the system was hydrolyzed by acetic acid for 2 min. The "toluene: acetic acid" mole ratio was 40:3. The obtained sol was labeled as Al_2O_3 (org). Preparation of magnesium hydroxide sol was performed using the metallic magnesium as precursor [23–25]. Magnesium ribbon (pretreated to eliminate the oxide film and cut into small pieces) was placed into flask with methanol. The mixture was stirred at 50 ℃ in an argon atmosphere. As a result, magnesium methoxide was formed. Toluene used as a dispersing agent was added to the obtained solution with "methanol:toluene" volume ratio of 1:3. Then, the solution was hydrolyzed dropwise by water at room temperature thus resulting in formation of opalescent sol labeled as $Mg(OH)_2$ (org). Silica sol was prepared via tetraethoxysilane (TEOS) route. TEOS was heated up to 80 ℃ in a beaker. Then, purified ethanol was added in a ratio $m(C_8H_{20}O_4Si)$:$m(C_2H_5OH)$= 1:1, and the mixture was stirred for 30 min. Finally, 30% solution of ethanol in water with pH = 3 (provided by addition of concentrated hydrochloric acid) was added into the beaker. The hydrolysis of TEOS was carried out during 3 h. The obtained sol was named as SiO_2 (org). In aim to prepare cordierite from organic precursors, sols described above were mixed in the following order thus preventing coagulation of the system: silica sol was mixed with magnesium hydroxide sol, and then alumina sol was added slowly and dropwise. The amounts of components were taken in order to obtain 0.349 g of Al_2O_3, 0.514 g of SiO_2, and 0.137 g of MgO for 1 g of cordierite.

Preparation details and characteristics of obtained sols are summarized in Table 1. Each three-component system (inorganic and organic) was stirred for 5 h, resulting in formation of stable Al–Si–Mg gel. Particle size distributions of sols were measured using a Malvern Zetasizer Nano ZS instrument.

The gels were dried under different conditions. The xerogels were obtained by drying gels under normal conditions in air. The aerogels (AP—aerogel prepared) were prepared by drying gels under supercritical conditions. In this case, the gels were placed into an autoclave (Autoclave Engineers EZE-Seal) and slowly heated up to 240 ℃ with temperature ramping rate of 3 ℃/min. The pressure inside autoclave has reached the value of 65 atm. Then, the dispersion medium was quickly released.

After drying, the xero/aerogels were dissolved in

Table 1 Characteristics of alumina, silica, and magnesia sols

Sol*	Precursor	Dispersion medium	Hydrolyzing agent	Specific weight of disperse phase $\omega \pm \Delta$ (%)	Density $\rho \pm \Delta$ (g/cm^3)	Dynamic viscosity $\eta \pm \Delta$ (mPa·s)	Average particle size $D \pm \Delta$ (nm)
Al_2O_3 (org)	Aluminium ethoxide	Ethanol	Water	6.1 ± 0.3	0.86 ± 0.01	—	71.0 ± 3.0
Al_2O_3 (inorg)	Aluminium chloride hexahydrate	Water	Ammonia solution	3.4 ± 0.3	1.03 ± 0.02	1.35 ± 0.05	67.0 ± 3.0
SiO_2 (org)	Tetraethoxysilane	Ethanol	Hydrochloric acid solution	14.1 ± 0.6	0.89 ± 0.02	1.61 ± 0.06	11.3 ± 1.8
SiO_2 (inorg)	Sodium metasilicate	Water	Hydrochloric acid solution	5.1 ± 0.6	1.05 ± 0.02	1.32 ± 0.05	32.5 ± 2.1
$Mg(OH)_2$ (org)	Magnesium methoxide	Toluene	Water	1.98 ± 0.13	0.85 ± 0.02	—	97.0 ± 4.0

*Org—the sols obtained from organic precursors; inorg—the sols obtained from inorganic precursors.

5 wt% polyvinyl alcohol (PVA) solution and casted on a macroporous ceramic cordierite support by dipping for 10 s. All membrane samples were dried at 40 ℃ until the weight of the membrane remained constant. Further calcinations were carried out at temperatures ranging from 40 to 1200 ℃, and the samples were kept in a furnace for 2 h.

Chemical analysis of natural raw materials was carried out by means of MESA 500W X-ray fluorescence analyzer (Horiba). Scanning electron microscopy (SEM) images were collected on a JEOL JSM-6460 scanning electron microscope. X-ray diffraction (XRD) analysis was conducted on a Shimadzu XRD-6000 fitted with a Cu Kα radiation source. Calorimetric experiments were performed with a differential scanning calorimeter Netzsch STA 409 PC/PG with a heating rate of 5 ℃/min. In order to study the effect of precursor's nature, drying and calcination conditions on textural properties of the samples, xerogel and aerogel powders treated at 200 ℃ and ceramic discs with supported microporous layer calcined at 1200 ℃ were examined. Measurements of the surface area as well as micro/mesopore analysis were carried out by means of ASAP 2400 instrument. Prior to the experiment, the sample was degassed at 150 ℃ for a few hours under dynamic vacuum of 10^{-5} Torr until no gas release from the sample was detected. Measurement of the surface area and macropore analysis of cordierite ceramic were carried out by means of AutoPore IV 9500 V1.09.

3 Results and discussion

According to the XRD data (Fig. 2), the main identifiable phases for cordierite ceramics prepared from natural raw materials are $Mg_2Al_4Si_5O_{18}$ cordierite (JCPDS No. 13-294) and spinel $MgAl_2O_4$ (JCPDS No. 21-1152). The content of spinel in the sample is less than 7%.

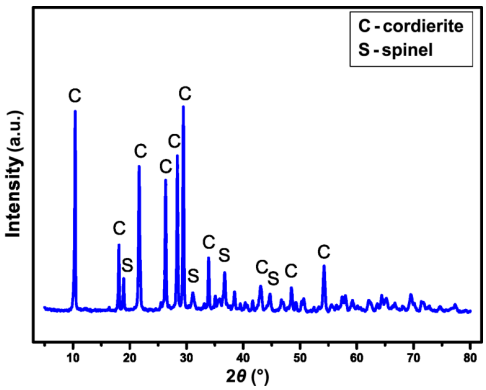


Fig. 2 XRD pattern of the cordierite ceramic.

Figure 3 shows the SEM images of the porous cordierite ceramic. As seen from the images, the pore size is seemed to be in a range of 5–15 μm. According to mercury porosimetry (Fig. 4), the ceramic is characterized by a narrow distribution of pore size and the average pore size is equal to 9.5 μm. Open porosity of ceramic is estimated to be 30%.

DSC and DTG curves of samples prepared by sol–gel method from organic or inorganic precursors under different drying conditions are given in Fig. 5. It helps us to choose the optimal heating treatment mode which is required to avoid some undesirable effects taking place during the calcination procedure (cracking, shrinkage, etc.).

In the case of organic precursors (Fig. 5(a)), an endothermic peak below 200 ℃ is observed. It corresponds to elimination of residual dispersive media (ethanol, toluene). This peak is absent when the supercritical drying is applied and the most part of dispersive agents are being removed (Fig. 5(b)). The mass changes in TG curves (Figs. 5(a) and 5(b)) at temperatures up to 700 ℃ can be assigned to removal of structural water and transformation of hydrated (hydroxide) species into oxide ones. Minor peaks in a

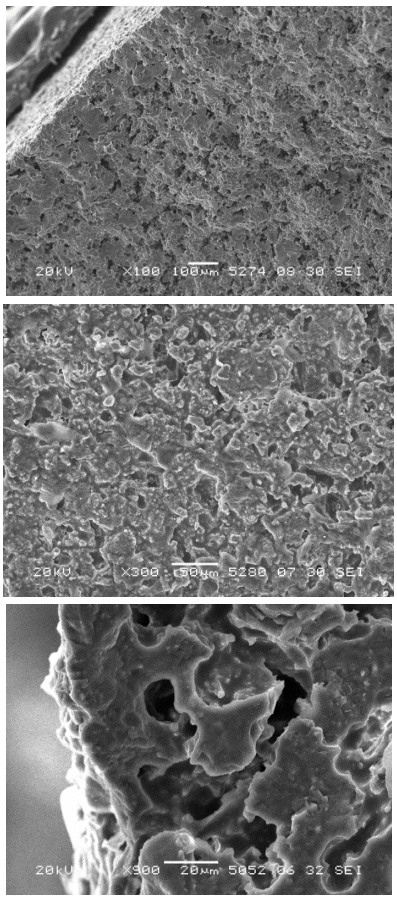


Fig. 3 SEM images of the porous cordierite ceramic.

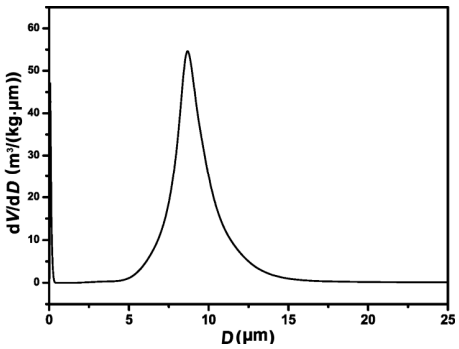


Fig. 4 Mercury porosimetry curve of the cordierite ceramic.

region of 900–1250 ℃ are associated with the formation of cordierite when metastable μ-cordierite transforms into α-modification of cordierite confirmed by XRD data. Increasing the temperature up to 1300 ℃ leads to formation of the primary liquid phase of eutectic composition (19.3% MgO, 17.3% Al_2O_3, 63.4% SiO_2) which is characterized by low density. The amount of this phase increases rapidly with temperature growth thus governing very short interval of vitrified state. At a temperature above 1430 ℃, the cordierite undergoes melting with formation of mullite and magnesia glass.

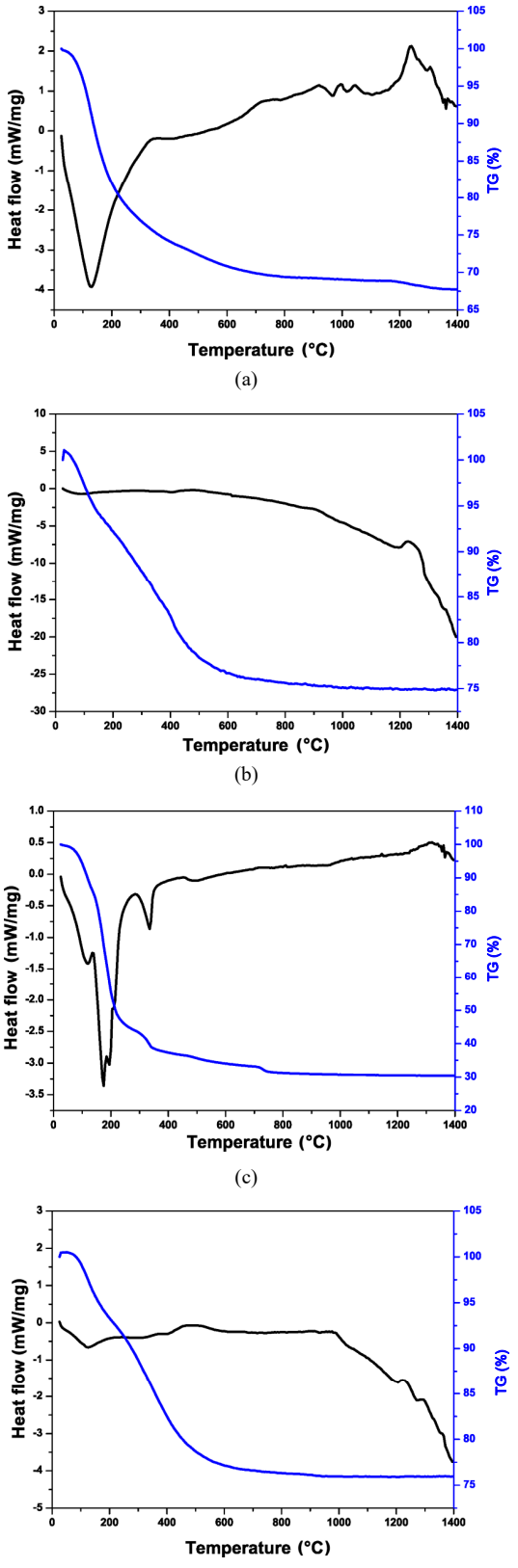
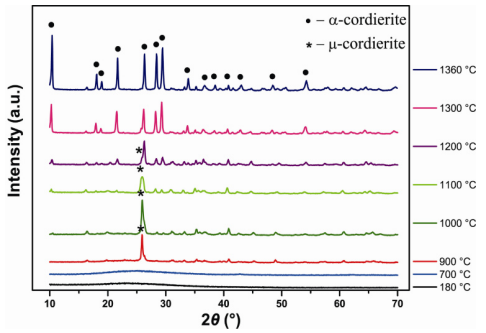


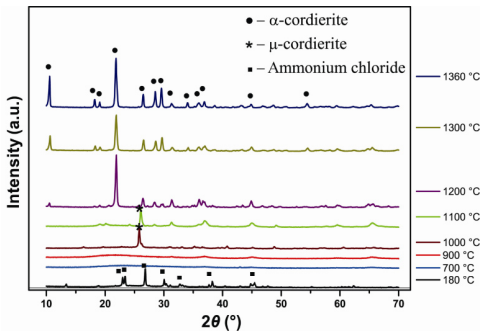
Fig. 5 DTG and DSC curves for $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ ceramics prepared from (a, b) organic and (c, d) inorganic precursors. Curves in (b) and (d) correspond to the samples dried in the supercritical conditions.

In the case of inorganic precursors (Fig. 5(c)), the endothermic peaks below 450 ℃ correspond to water elimination and ammonium chloride decomposition. The latter is believed to be formed as a result of aluminum and magnesium chloride hydrolysis in a presence of ammonia. Absence of these peaks in DSC curve for the sample dried in supercritical conditions (Fig. 5(d)), similarly to the previous case, is connected with preliminary removal of water and dissolved ammonium chloride during the drying procedure. Further behavior of the samples during the thermal analysis (TG curves in Figs. 5(c) and 5(d)) can be explained by hydroxide/oxide transformations (below 700 ℃) and cordierite formation (900–1250 ℃).

XRD patterns for the samples treated at 180, 700, 900, 1000, 1100, 1200, 1300, and 1360 ℃ are shown in Fig. 6. Diffraction patterns for the samples calcined at 700 ℃ are very similar between themselves, indicating amorphousness of the samples. In the case of organic derived samples (Fig. 6(a)), some evidence for reflections that correspond to μ-phase of cordierite (JCPDS No. 14-249) is observed in the range of calcination temperature from 900 to 1300 ℃. Peaks in the pattern for the sample treated at 1360 ℃ can be attributed to stable α-phase of cordierite (JCPDS No. 13-294), while presence of μ-phase is not observed.



(a)



(b)

Fig. 6 XRD patterns of the samples prepared from (a) organic and (b) inorganic precursors.

In the case of sample prepared from inorganic precursors and treated at 180 ℃ (Fig. 6(b)), diffraction pattern is typical and corresponds to ammonium chloride (JCPDS No. 34-710). Formation of μ-phase of cordierite is observed only in a range of 1000–1100 ℃, while at 1200 ℃ it is almost completely disappeared. Patterns for the samples calcined at 1200 ℃ and above have the peaks corresponding to α-phase of cordierite only. It can be concluded here, that the calcination temperature of 1200 ℃ is enough for inorganic derived samples.

Additionally, it can be mentioned that treatment at temperature above 1200 ℃ also results in a texturing (preferential orientation of crystallites) which changes the intensity of the corresponding peaks in XRD patterns of the samples obtained from inorganic precursors if comparing with organic derived samples and JCPDS No. 13-294. Particularly, an increase of peak intensity for (112) as well as overall reduction of relative intensities in comparison to (110) can be observed [26–29].

The textural characteristics of the xerogel and aerogel powders treated at 200 ℃ are reported in Table 2. The obtained samples are characterized by unique textural properties and high surface area. In the case of AP samples, the values of surface area are two times higher comparing with that of the conventionally prepared ones. Aerogel technology is known to prevent the formation of liquid–vapor meniscuses at the exit of the gel pores responsible for a mechanical tension in the liquid and a pressure on the pore walls, which induce gel shrinkage, thus avoiding collapse of the pore structure [6]. Moreover, a supercritical fluid can be evacuated as a gas leaving the initial wet material in the form of dry solid skeleton. The samples obtained by this approach are characterized by a very open porous structure, which is similar to the initial gel structure [30].

Coating of macroporous cordierite ceramic with $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ layer followed by sintering at

Table 2 Textural characteristics of the xerogel and aerogel powders treated at 200 ℃

Sample	Surface area S_{BET} (m^2/g)	Pore volume V_{pore} (cm^3/g)	Pore diameter D_{pore} (nm)
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (org)	348	0.23	2.6
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (orgAP*)	727	0.49	2.7
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (inorg)	156	0.65	16.6
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (inorgAP*)	384	1.12	11.6

*AP—aerogel prepared.

1200 ℃ has allowed us to prepare the ceramic membranes of asymmetric type. As a result of this thermal treatment, the sol–gel prepared layer becomes fritted and strongly affixed to the ceramic support. SEM images shown in Fig. 7 reveal that the thickness of micro/mesoporous layers lies in a range of 20–30 μm. The layers are represented by the agglomerates of small particles with fine structure, when the hollows between particles create the porous structure. The results of porosity measurement are demonstrated in Table 3 and Fig. 8. As it follows from Fig. 8, the pore volume distribution for the samples derived from organic precursors is narrow, and lies near 4 nm. In the case of conventionally prepared sample (Fig. 8(a)), small shoulder in a range of 5–8 nm is presented in the curve. Polydisperse (Fig. 8(c)) and wide (Fig. 8(d)) pore volume distributions observed in the case of the samples from inorganic precursors are connected with effect of ammonium chloride on formation of porous structure during the thermal treatment procedure.

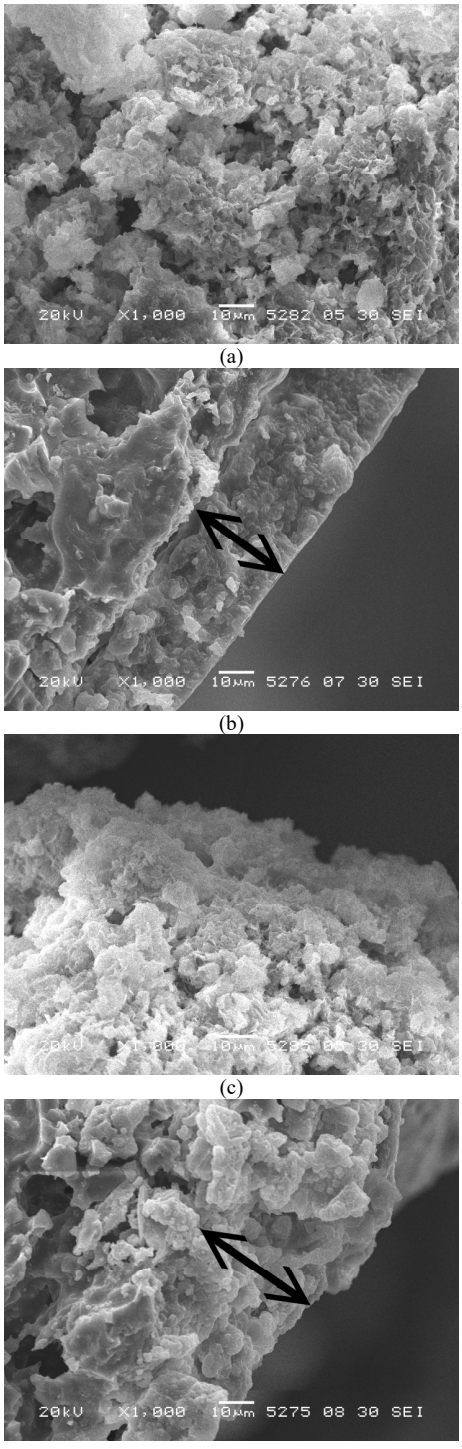


Fig. 7 SEM images of (a, c) surface and (b, d) cross-section of the $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ ceramics prepared from (a, b) organic and (c, d) inorganic precursors and dried in the supercritical conditions.

Thereby, the use of different precursor of alumina does not make a significant contribution in characteristics of individual sols. Both the stability and particle size of colloidal systems are of the same level. At the same time, particle size of silica is shown to be reduced about three times when TEOS is used as a precursor. It strongly affects the pore size of final cordierite ceramics while silica content exceeds 60% of its composition. An increase of surface area of 1.5 times (see Table 3) indicates that organic compounds used act as additional pore-forming agents thus resulting in formation of more friable and permeable structure. Short-term elimination of dispersive media in a regime of autoclave drying maintains the micro/mesoporous structure which leads to an increase of surface area values more than 2 times if comparing with conventional drying in a muffle.

Table 3 Textural characteristics of the $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ layers after sintering at 1200 ℃

Sample	Surface area S_{BET} (m^2/g)	Pore volume V_{pore} (cm^3/g)	Pore diameter D_{pore} (nm)
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (org)	52	0.08	6.0
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (orgAP*)	107	0.17	4.4
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (inorg)	30	0.54	15.7
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ (inorgAP*)	69	0.89	9.1

*AP—aerogel prepared.

4 Conclusions

In this work, the asymmetric systems based on cordierite with hierarchical porous structure were obtained by combination of ceramic and sol–gel technologies. The ceramic support prepared from natural raw materials is characterized by narrow pore

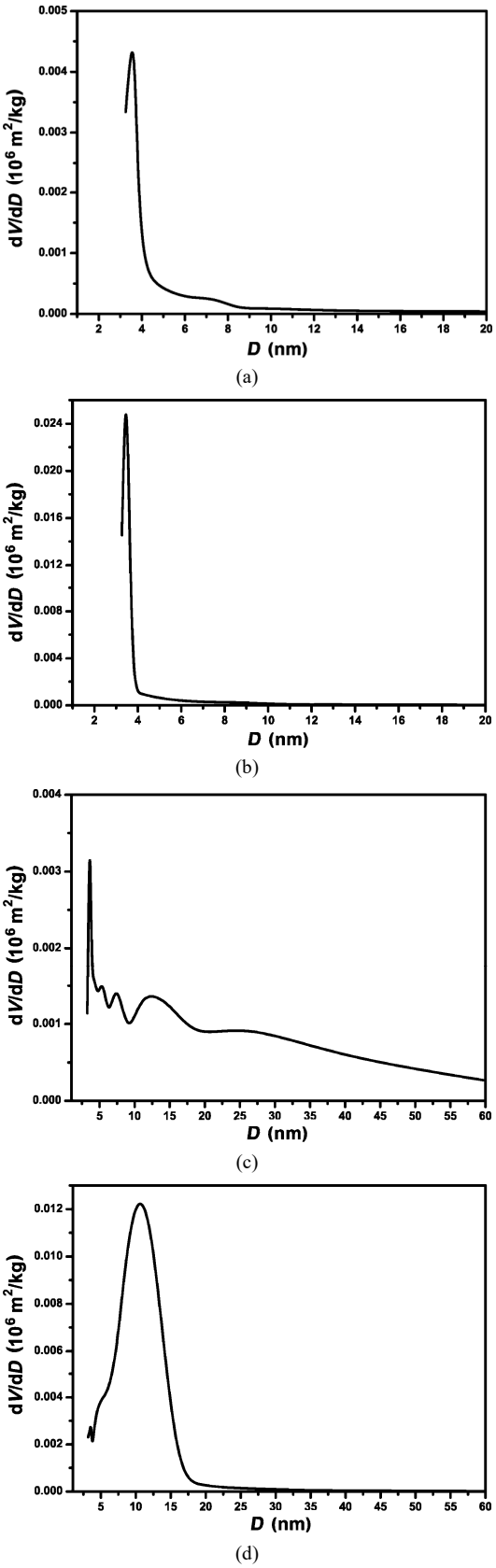


Fig. 8 Pore volume distribution calculated from desorption branch of the isotherm for the $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ layers: (a) org, (b) orgAP, (c) inorg, (d) inorgAP.

size distribution in a range from 5 to 15 μm. The variation of precursor's nature and drying conditions for sol–gel system allows one to create mesoporous layers with controllable textural parameters. Supercritical drying leads to an increase of surface area of cordierite layer more than 2 times. The prepared asymmetric systems can be applied as chemically and thermally stable membranes and catalyst's supports.

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